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Unimolecular reaction dynamics from kinetic energy release distributions. VI. Energy-selected ions

J.C. Lorquet

Département de Chimie, Université de Liège, Sart-Tilman (B6), B-4000 Liège 1, Belgium

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Abstract

The kinetic energy distribution (KERD) determined by Brand et al. [Chem. Phys. 76 (1983) 111] for the iodine loss from energy-selected iodopropane ions has been analyzed by the maximum entropy method. The entropy deficiency DS has been determined and the value of $e^{-\mathrm{DS}}$, which measures the efficiency of phase-space sampling, has been found equal to about 96%, thus corresponding to a nearly fully statistical situation. The phase space theory of Klots describes a slightly more constrained situation with $e^{-\mathrm{DS}} \approx 77\%$. A rapid determination of the sampled fraction of phase space is possible from energy-selected KERDs, based on the fact that there exists a direct relationship between the efficiency $e^{-\mathrm{DS}}$ and the reduced maximum of the KERD $\epsilon^M_{\mathrm{red}} = \epsilon^M(E)/\langle\epsilon\rangle_E$. The product $\epsilon^M(E)\,P(\epsilon^M|E)$ or $\epsilon^M_{\mathrm{red}}P(\epsilon^M_{\mathrm{red}})$ holds the same property. (Int J Mass Spectrom 201 (2000) 59–67) © 2000 Elsevier Science B.V.

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1. Introduction

How can one assess the validity of statistical theories of unimolecular decay from a study of the corresponding translational kinetic energy release distributions (KERDs) [1–8]? The version of phase space theory incorporating Langevin long-range forces derived by Klots [9–12] has been extensively used [1,3,6,13–20]. Its validity is based on several assumptions. First, that a statistical model be applicable, i.e. that the ergodic hypothesis be satisfied, in other words that phase space be uniformly sampled. Second, that the dissociation dynamics be described by a two-body, central field model, with a loose transition state related to a centrifugal barrier. Third, that the isotropic long-range $-R^{-4}$ (Langevin) law be valid and that the vibrational–rotational couplings be negligible all the way from infinity down to the region of the potential energy surface where the energy partitioning among products is determined. Although plausible and frequently remarkably successful, these assumptions are obviously questionable. The purpose of the present series of articles is to investigate the validity of the first one of them, concerning the validity of the ergodic hypothesis.

Very often, the measured distributions have a very simple shape, exhibit no structure, and are determined with a limited accuracy. Clearly, a restricted amount of information can be extracted from them, and the main danger is to push the data analysis a bit too far.

There exists a very general mathematical method

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* Corresponding author. E-mail: jc.lorquet@ulg.ac.be

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derived from information theory, called the maximum entropy method [21], whose aim is precisely to derive the least biased inference. In its applications to chemical physics, it has been designed to discern the influence of nonstatistical effects in product energy distributions [19,22–34], where it has met with great success. However, its aim is not to calculate from first principles a KERD deduced, e.g. from the value of the polarizability of the neutral fragment and from vibrational frequencies and rotational constants. Instead, it involves a comparison between the experimental data and a so-called prior distribution. The latter represents the most statistical distribution at a given internal energy E, and is obtained from a calculation of the density of states, $N(E)$. From a comparison between an experimental result and the prior distribution, a so-called entropy deficiency is obtained, which is related to the discrepancy between the actual situation and that predicted by the most statistical estimate. In this way, a maximum entropy analysis checks the basic assumption of any statistical theory, i.e. estimates the efficiency of phase space sampling.

2. Energy selected fragmentation

KERDs can be derived by scanning metastable dissociation signals recorded in a two-sector mass spectrometer. Then, they do not correspond to a well defined internal energy, but to a distribution of internal energies, denoted $T(E)$. This method has been used in the first articles of this series [30–32]. However, photoion–photoelectron coincidence (PIPECO) detection techniques [6,7,35,36] allow the measurement of translational energies resulting from the dissociation of energy-selected molecular ions.

In this way, KERDs can be determined at specified values of E and are denoted $P(\epsilon|E)$, where E is the energy in excess of the dissociation threshold. They can also be studied on a reduced scale, i.e. plotted as a function of a reduced energy parameter, ϵ_{red}. Powis and co-workers [7,19] have advocated the very natural choice $\epsilon_{\mathrm{red}} = \epsilon/E$. Alternatively, Baer and co-workers [14,15] have adopted the average translational kinetic energy $\langle\epsilon\rangle$ (i.e. the first moment of the distribution) as an appropriate scaling parameter. The maximum entropy equations reported in Sec. 3 [Eqs. (1)–(14)] can be scaled in either way, under certain specified conditions.

3. Maximum entropy method

Let us start by defining the most possible statistical KERD, denoted "the prior distribution" and defined as the expected distribution if all quantum states at energy E were populated with equal probability. Denoting densities of states by $N(E)$, one has [1,22–25,30–32,37,38]:

$$P^0(\epsilon|E) = A(E)\epsilon^{1/2}N(E-\epsilon) \tag{1}$$

where $N(E - \epsilon)$ denotes the density of rovibrational states of the pair of fragments.

The KERD can also be expressed as a function of a reduced variable ϵ_{red}, varying in the range $[0, E_{\mathrm{red}}]$. Two possibilities are offered. Powis and co-workers [7,19] recommend $\epsilon_{\mathrm{red}} = \epsilon/E$ with $E_{\mathrm{red}} = 1$. Then

$$P^0(\epsilon|E) = A'(E)\epsilon_{\mathrm{red}}^{1/2}N[E(1-\epsilon_{\mathrm{red}})] \tag{2}$$

Baer and co-workers [14,15] propose, as an alternative choice, $\epsilon_{\mathrm{red}} = \epsilon/\langle\epsilon\rangle$ with $E_{\mathrm{red}} = \mathrm{E}/\langle\epsilon\rangle$. Then

$$P^0(\epsilon|E) = A''(E)\epsilon_{\mathrm{red}}^{1/2}N[E(1-\epsilon_{\mathrm{red}}\langle\epsilon\rangle/E)] \tag{3}$$

$A(E)$, $A'(E)$, and $A''(E)$ are normalization factors determined by the condition:

$$\int_0^{\mathrm{E}} P^0(\epsilon|E)\, d\epsilon = \int_0^{E_{\mathrm{red}}} P^0(\epsilon_{\mathrm{red}})\, d\epsilon_{\mathrm{red}} = 1 \tag{4}$$

In this article, three possible empirical parameterizations have been tried for the function $N(E)$:

$$N(E) = C\exp(\alpha E) \tag{5}$$

$$N(E) = CE^s \tag{6}$$

$$N(E) = C\exp(\beta E^{1/2}) \tag{7}$$

where C, α, β, and s are empirical parameters to be fitted to an actual calculation of the density of states by, e.g. the Beyer-Swinehart algorithm [1,39,40] applied to a set of ab initio calculated vibrational frequencies. According to our experience, the third parametrization appears to be quite realistic.

By definition, in information theory, the prior distribution is that of maximum entropy. The purpose of the method is to compare it with the actual situation, in order to detect the influence of constraints in the dynamics which are responsible for incomplete phase space sampling. The comparison leads to a so-called entropy deficiency, denoted DS. The quantity $e^{-\mathrm{DS}}$ plays a fundamental role in what follows. It can be shown to represent the fraction of phase space actually sampled [30–33,41,42]. Loosely stated, it measures the efficiency of energy "scrambling" or "randomization" postulated by statistical theories. It can be referred to as an "ergodicity index" and is therefore directly related to the applicability of statistical theories.

What are the constraints that act on the dynamics and therefore that are able to perturb a statistical treatment? Previous studies in this vein [30–32,34] have been unable to detect any constraint other than that provided by the momentum gap law [43–45], which applies to all vibrational predissociation processes [26,31,32,46]. This can be understood as follows. Fundamentally, a unimolecular dissociation is a vibrational predissociation process [47]. In quantum mechanics, the momentum gap law results from the analytical expression of the oscillatory wave function that describes the translational motion of the pair of fragments as they separate [31,32,43–45]. In classical mechanics, this law is related [26] to the Franck-Condon principle, which says that the nuclei are able to change their momenta only reluctantly. Therefore, there exists a systematic effect that prevents the energy partitioning between the reaction coordinate and the subset of internal ro-vibrational modes from being fully statistical. More explicitly, the energy E in excess of the dissociation threshold is preferentially released into rotational or vibrational energy of the separating fragments. Hence, less translational energy is channeled into the reaction coordinate than the statistical estimate. In the maximum entropy language, the dynamical constraint bears on the linear momentum, i.e. involves the square root of the translational energy ϵ. It then follows that, for reactions that proceed with no reverse activation barrier, the actual KERD is related to the prior distribution via the following equation [30–32,34]:

$$P(\epsilon|E) = P^0(\epsilon|E)\ \exp(-\lambda_0)\ \exp(-\lambda_1\epsilon^{1/2}) \tag{8}$$

In this equation, λ_1 is a Lagrange multiplier directly related to the nonstatistical nature of the reaction, while the factor $\exp(-\lambda_0)$ can be determined by normalizing the actual KERD:

$$\int_0^{E} P(\epsilon)\ d\epsilon = 1 \tag{9}$$

In dimensionless reduced units, one has

$$P(\epsilon_{\mathrm{red}}) = P^0(\epsilon_{\mathrm{red}})\ \exp(-\lambda_0)\ \exp[-\lambda_1\epsilon_{\mathrm{red}}^{1/2}] \tag{10}$$

Note, however, that the Lagrange parameters λ_0 and λ_1 do not assume the same numerical values in Eqs. (8) and (10). In Eq. (10) they are now dimensionless quantities. The first one (i.e. λ_0) is determined by the condition

$$\int_0^{E_{\mathrm{red}}} P(\epsilon_{\mathrm{red}})\ d\epsilon_{\mathrm{red}} = 1 \tag{11}$$

Scaling (and use of reduced energy units) is possible in an energy range where the parameters that determine $N(E)$ (i.e. α, s, or β, as the case may be) as well as the Lagrange parameter λ_1 remain constant.

The average energy is given by the first moment of the KERD, i.e. by

$$\langle\epsilon_{\mathrm{red}}\rangle = \int_0^{E_{\mathrm{red}}} \epsilon_{\mathrm{red}}P(\epsilon_{\mathrm{red}})\ d\epsilon_{\mathrm{red}} \tag{12}$$

In order to assess the validity of a statistical model, one has to determine the entropy deficiency via a comparison between $P(\epsilon_{\mathrm{red}})$ and $P^0(\epsilon_{\mathrm{red}})$, i.e. one has to calculate

$$\mathrm{DS} = -\lambda_0 - \lambda_1\langle\epsilon_{\mathrm{red}}^{1/2}\rangle \tag{13}$$

where $\langle\epsilon_{\mathrm{red}}^{1/2}\rangle$ is the average of the constraint $\epsilon_{\mathrm{red}}^{1/2}$ over the KERD, i.e.

$$\langle \epsilon_{\mathrm{red}}^{1/2} \rangle = \int_0^{E_{\mathrm{red}}} \epsilon_{\mathrm{red}}^{1/2} P(\epsilon_{\mathrm{red}})\, d\epsilon_{\mathrm{red}} \tag{14}$$

When the simple parametric expressions given in Eqs. (5)–(7) are adopted for the density of states, it is possible to integrate Eqs. (9) and (11)–(14) analytically [although the use of Eq. (7) leads to mathematical complications]. Closed-form expressions for the moments of the distribution as well as for its maximum $\epsilon_{\mathrm{red}}^{M}$ and for the entropy deficiency DS can thus be obtained. The results are expressed in terms of special functions like the parabolic cylinder or the generalized hypergeometric functions [48,49]. The details of the analytic calculation will not be given here because the evaluation of these special functions still requires numerical computations. (Nevertheless, a great simplification ensues compared with a full numerical treatment.) A second reason is that the procedure described in Sec. 5 provides a shortcut to computations.

4. Iodopropane ion

Brand et al. [14] have determined the KERD in the fragmentation of energy-selected iodopropane ions:

$$C_3H_7I^+ \rightarrow C_3H_7^+ + I \tag{15}$$

The internal energy range studied extends up to 3 eV above the dissociation threshold. The measurements have been carried out for two isomers but generate a unique KERD when presented in reduced units ($\epsilon_{\mathrm{red}} = \epsilon/\langle\epsilon\rangle$).

High-quality ab initio calculations [50,51] have later on established that the $C_3H_7^+$ ion is characterized by two structures. The most stable minimum of its potential energy surface corresponds to the 2-propyl cation with insignificant methyl rotation barriers. About 0.3 eV above comes a less stable minimum corresponding to a protonated cyclopropane structure. The 1-propyl cation conformation is not a stable minimum, but a transition state connecting the two previous structures and located 0.84 eV above the deepest minimum. Although already available in the literature [51], the calculation [52] of the vibrational frequencies of these three stationary points has been repeated at the B3-LYP/6-31G* level recommended by Scott and Radom [53]. The lowest two torsional frequencies have been replaced by free rotors. The CH bending mode at 710 cm^{-1} was deemed responsible for the isomerization motion and hence treated as an anharmonic oscillator with levels converging at 0.84 eV. Based on these data, the density of rovibrational states of the $C_3H_7^+$ fragment was calculated by the Beyer-Swinehart algorithm [1,39,40] and fitted to the three empirical equations (5)–(7). As expected, the best fit was provided by Eq. (7). In the energy range (0–1.4 eV) this procedure generated the following approximate equation [with E in eV and $N(E)$ in inverse wave number units]:

$$N(E) = 34.728 \exp(18.984 E^{1/2}) \tag{16}$$

At energies larger than 1.4 eV, the following expression is more accurate:

$$N(E) = 92.749 \exp(18.157 E^{1/2}) \tag{17}$$

The available experimental data (Fig. 3 of [14]), determined for all energies and for both isomers as a function of the reduced variable $\epsilon_{\mathrm{red}} = \epsilon/\langle\epsilon\rangle$, have been fitted to Eq. (10) by a least-squares method. A value of $e^{-\mathrm{DS}} \approx 96\%$ is obtained. This value is not extremely accurate, because of the dispersion of the experimental data. Nevertheless, it indicates a nearly fully statistical situation.

The KERD predicted by phase space theory (Fig. 3 of [14]) also satisfactorily fits the currently available data. When analyzed by the maximum entropy equations [i.e. when fitted to Eq. (10) in order to compare it with the prior distribution], the KERD calculated by the Langevin model is found to describe a slightly more constrained situation with $e^{-\mathrm{DS}} \approx 77\%$.

In addition, Brand et al. have also measured the average kinetic energy $\langle\epsilon\rangle$ released as a function of the total energy E and have compared their measurements with statistical calculations. They observe a difference in the behaviour of the 1- and 2-isomers and note that, in the case of the 2-iodopropane ion, the measured average energy release exceeds the statistical estimate

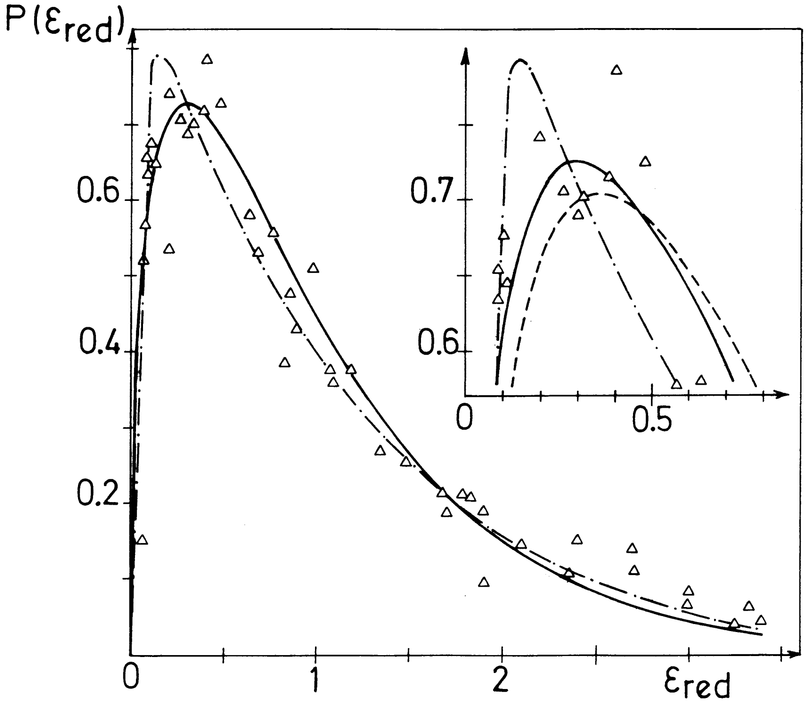

Fig. 1. Normalized KERD in reduced units ($\epsilon_{\text{red}} = \epsilon/\langle\epsilon\rangle$) for reaction $C_3H_7I^+ \rightarrow C_3H_7^+ + I$. Triangles: experimental data of [14] for both isomers at all energies. Solid line: least-squares fit to the maximum entropy Eq. (10), leading to an ergodicity index of 0.96. Dashed-dotted line: predictions of phase-space theory ([14]) ($e^{-DS} = 0.77$). Dotted line in the inset: prior (i.e. most statistical) distribution (corresponding to full phase space sampling).

calculated by them (Fig. 4 of [14]). These results have been compared with those deduced as follows from the maximum entropy method. The first moment of a KERD has been evaluated as a function of E with that value of λ_1 corresponding to $e^{-DS} = 0.96$. Thus, no difference is made in the calculations between 1- or 2-iodopropane. Our results, reported in Figs. 1 and 2, agree with the observed general average behaviour of both isomers.

5. Remarkable dimensionless expressions

When the KERDs are determined by scanning metastable dissociation signals, one has to carry out a tedious integration over a distribution of internal energies, as exemplified in the first articles of this series [30–32]. This step is obviously no longer necessary when the molecular ions are energy selected. One of the purposes of the present article is to show that the effort of selecting the internal energy generates a bonus. For reactions with no reverse activation barrier, a rough estimate of the efficiency of phase space sampling can be quickly obtained without carrying out the calculations and fits described in Sec. 4, thus without any precise knowledge of the rovibrational density of states of the pair of fragments.

The trick involves consideration, at a given energy, of dimensionless products or ratios of characteristic parameters of the KERD, like $\langle\epsilon\rangle/E$ (i.e. the ratio of the mean translational energy release to the excess energy) or $\langle\epsilon^2\rangle/(\langle\epsilon\rangle)^2$ (i.e. the ratio between the second moment and the square of the first moment of the KERD). The analytic expression of these ratios depends on two kinds of variables. First, on the parameters which determine the shape of the density of states of the fragments $N(E)$ [i.e. the parameters α, s,

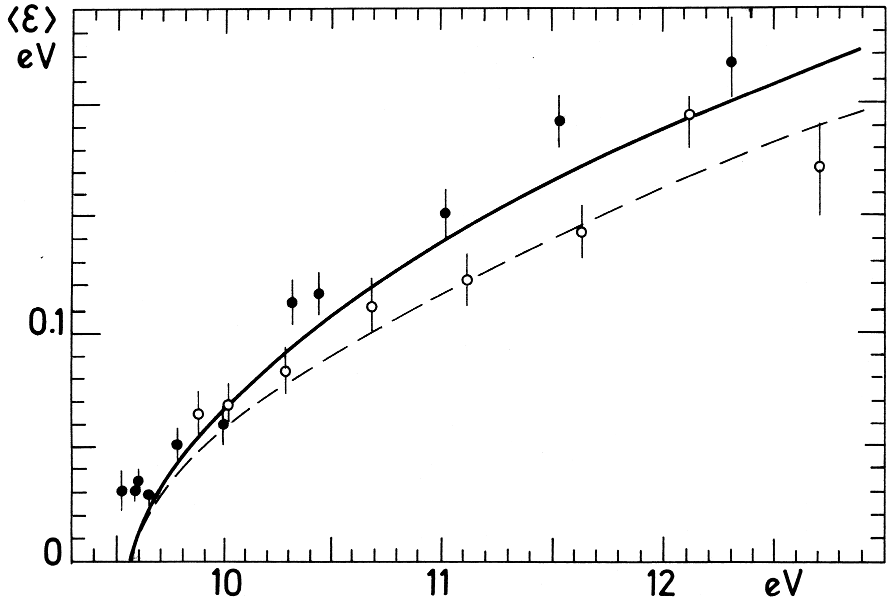

Fig. 2. KERD for reaction $C_3H_7I^+ \rightarrow C_3H_7^+ + I$ as a function of the absolute 0 K energy. Open symbols: experimental data of [14] for 1-iodopropane. Closed symbols: same for 2-iodopropane. Solid line: first moment of the maximum entropy distribution with a value of λ_1 corresponding to a 96% efficiency of phase-space sampling. Dotted line: predictions of phase-space theory ([14]).

or β defined in Eqs. (5)–(7); these parameters are directly related to the slope of $N(E)$ when plotted on a logarithmic scale]. Second, they also depend on the parameter which measures the nonstatistical behaviour, i.e. either λ_1, DS, or $e^{-\mathrm{DS}}$.

However, much to our surprise, two interesting dimensionless combinations were observed to depend only weakly on the exact shape of the function $N(E)$, i.e. on the value of the parameters α, s, or β.

The translational energy (scaled with respect to the average kinetic energy $\langle\epsilon\rangle$) at which the KERD admits its maximum, i.e. the ratio $\epsilon^M(E)/\langle\epsilon\rangle_E = \epsilon^M_{\mathrm{red}}$ is found to be fairly independent of the parametrization of the function $N(E)$. Therefore, it is directly related to quantity $e^{-\mathrm{DS}}$, as shown in Fig. 3.

Additionally, the dimensionless quantity $\epsilon^{\mathrm{M}}(E)\,P(\epsilon^M|E)$ or $\epsilon^M_{\mathrm{red}}\,P(\epsilon^M_{\mathrm{red}})$ is observed to be even more independent of the shape of the function $N(E)$ and thus to provide directly a good estimate of $e^{-\mathrm{DS}}$, i.e. of the sampled fraction of phase space, as shown in Fig. 4.

Thus, Figs. 3 and 4 allow a rapid determination of the efficiency of phase space sampling, practically without any knowledge of the function $N(E)$ and of the internal energy E. Unfortunately, the relationship holds only for reactions with no reverse activation barrier, when the ions are energy-selected and, it will be recalled, when the KERDs are normalized according to Eq. (9) or (11).

For example, in the case of $C_3H_7I^+$, one has $\epsilon^M_{\mathrm{red}} \approx 0.3$ and $P(\epsilon^M_{\mathrm{red}}) \approx 0.725$. When carried forward to Figs. 3 and 4, these values confirm the previous estimate $e^{-\mathrm{DS}} \approx 0.96$.

6. Discussion

Reaction (15) has been studied by two different approaches: the maximum entropy method and the orbiting transition state phase space theory (denoted OTS/PST in short [1]). Both involve approximations and comparing them is a delicate exercise.

The two methods differ in their philosophy. The OTS/PST requires the input of calculated frequencies,

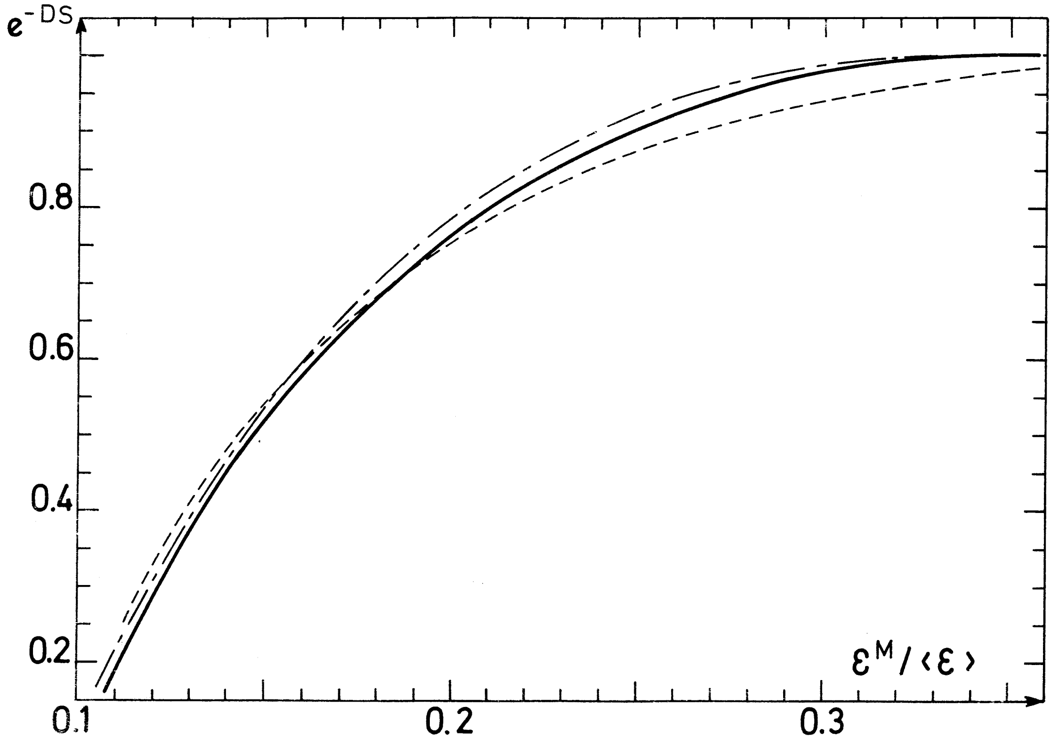

Fig. 3. Relationship between the efficiency of phase space sampling ($e^{-\mathrm{DS}}$) and the reduced maximum of the KERD $\epsilon^M_{\mathrm{red}} = \epsilon^M(E)/\langle\epsilon\rangle_E$ for various parametrizations of the density of states. Dashed-dotted line: exponential parametrization of $N(E)$ [Eq. (5)]. Dashed line: power law [Eq. (6)] with $s = 6$ (larger values of s lead to closer agreement with the exponential parametrization). Solid line: more realistic parametrization expressed by Eq. (7).

rotational constants and polarizabilities. From that knowledge, it is able to predict rate constants and KERDs. By contrast, the strategy of the maximum entropy method is entirely different. Vibrational frequencies and rotational constants are also required to calculate a density of states, but the latter is used to calculate a prior distribution as a reference (not as an approximation). Information about the magnitude of $e^{-\mathrm{DS}}$ is obtained via a comparison of the prior and the experimental distributions. No prediction is made. Thus, the maximum entropy method aims at interpreting whereas OTS/PST aims at predicting.

Both methods conclude that reaction (15) is very close to the statistical limit. However, the qualification “statistical” is understood in a different way in the two theories and the predicted curves for the statistical limit are different in the two models. In the maximum entropy method, the specification “fully statistical” implies perfect agreement with the prior distribution. However, the actual KERD is found to be slightly narrower and sharper than the prior distribution because the Lagrange parameter λ_1 [Eqs. (8) and (10)] assumes a positive value. As a result, the average release $\langle\epsilon\rangle$ (i.e. the first moment of the KERD) is lowered. This indicates a nonzero entropy deficiency and a slightly incomplete phase space sampling whose interpretation is not entirely clear. It might either result from the momentum gap law (as has been assumed here) or from constraints linked to conservation of angular momentum. However, the effect is small in the present case. This is related to the fact that in reaction (15), which involves the separation of two heavy fragments, one of them strongly polarizable, the conservation of angular momentum is probably not a severe constraint.

Clearly, the role played by angular momentum

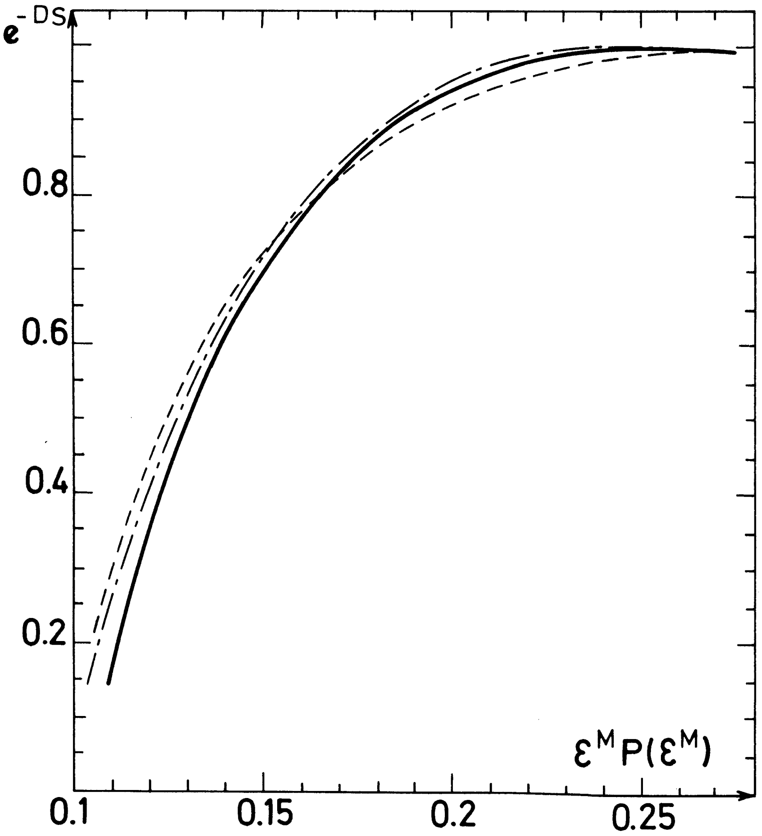

Fig. 4. Relationship between the efficiency of phase space sampling ($e^{-\mathrm{DS}}$) and the product $\epsilon^M(E)P(\epsilon^M|E)$ or $\epsilon^M_{\mathrm{red}}\ P(\epsilon^M_{\mathrm{red}})$ for various parametrizations of the density of states. Dashed-dotted line: exponential parametrization of $N(E)$ [Eq. (5)]. Dashed line: power law [Eq. (6)] with $s = 6$ (larger values of s lead to closer agreement with the exponential parametrization). Solid line: more realistic parametrization expressed by Eq. (7).

conservation in the maximum entropy method must be examined in more detail. It is related to the behaviour of the KERD around $\epsilon = 0$, which is accounted for in a different way in the two theories. The prior distribution goes to zero because the translations are treated as a three-dimensional energy sink. By contrast, in OTS/PST, the KERD dips to zero provided that centrifugal barriers are taken into account. Work in that direction has been attempted in the present laboratory.

7. Concluding remarks

The calculations reported in the present article describe in fact a fit of the experimental results obtained by Brand et al. to Eqs. (8) and (10) resulting from the maximum entropy theory. Since the starting point gathers data determined for all energies and both isomers, our results can only lead to an average entropy deficiency and are unable to report on any difference in behaviour between the two isomers.

Fig. 1 helps the practising mass spectrometrist to assess the difference between KERDs corresponding to a fully ergodic case (i.e. the prior distribution represented by the dashed line in the inset), a 93% efficiency of phase space sampling (the solid line representing the best fit to the experimental distribution using DS as a fitting parameter) and an efficiency reduced to 77% (the phase-space result represented by the dashed-dotted line). In particular, it helps to evaluate the difficulty to discern in practice among them when experimental uncertainties are taken into account.

A great simplification and an interesting control over the problem is provided by Figs. 3 and 4. Information on the validity of a statistical treatment can thus be obtained with a minimum knowledge of the KERD, since the calculation of the density of states $N(E)$ can be bypassed. Unfortunately, the relationship holds only when the ions are energy selected and for reactions with no reverse activation barrier.

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